Study of the colouring process in copper ruby glasses by optical and EPR spectroscopy

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The mechanism responsible for the development of the ruby colour in silica glasses containing copper have been investigated by means of optical and EPR spectroscopy. During the striking treatment, the evolution of the concentration of Cu^+ and Sn^{2+} has been followed through their luminescence bands, whereas the Cu^{2+} concentration has been monitored by the EPR spectra. To account for the data, a model for the colouring which involves two simultaneous redox reactions:

(i) $2Cu^+ \rightarrow Cu^{2+} + Cu^0$

(ii) $2Cu^{2+} + Sn^{2+} \rightarrow 2Cu^+ + Sn^{4+}$
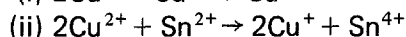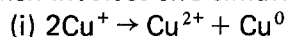
has been proposed. According to it, the role of tin is to act as a redox buffer to regenerate Cu^+, therefore favouring the coalescence of Cu_2O colloids.

1. Introduction

Optical properties of glasses containing copper have been extensively studied for a long time. Although many basic features are now well understood, some related problems are still an open question. The melting of copper ruby glasses and the development of the characteristic deep red colour during a heat treatment is one of these unsolved questions.

Several stringent conditions are required to obtain a good ruby glass, including copper concentration, glass composition, melting atmosphere and temperature and time of heat treatment. In particular, the addition of an adequate amount of tin appears necessary. Although the process is, indeed, technologically mastered, three basic questions still remain without an answer: (a) the physical-chemical mechanism controlling the colouring, (b) the chemical and crystallographic structure of the particles acting as colour centres and (c) the role of tin in the overall process of ruby colouration.

With regard to the nature of the colouring particles, it should be remarked that direct tech-niques such as X-ray diffraction, electron diffraction and transmission electron microscopy (TEM), have failed to provide an unambiguous answer. In fact, both Cu^0 and Cu_2O colloids have been invoked to account for the ruby colour of these glasses.

Several models have been proposed to explain the striking process. The three best established ones assume that copper is present as cuprous ions in the colourless chilled glass. The first one [1] proposes the following reaction:

$$2Cu^+ + Sn^{2+} \rightarrow 2Cu^0 + Sn^{4+} \qquad (1)$$
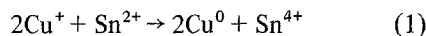
i.e. Cu^+ ions are reduced to Cu^0 by Sn^{2+} ions. The Cu^0 atoms thus produced aggregate into metallic colloidal particles responsible for the colouring.

A second model [2] involves the dismutation of Cu^+, i.e.

$$2Cu^+ \rightarrow Cu^0 + Cu^{2+} \qquad (2)$$
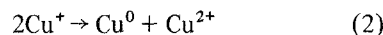
As in the previous model, the coalescence of Cu^0 produces optically active colloids accountable for the colour development.

Finally, a third model [3] proposes that, during

TABLE I Glass compositions

Glass	Base composition (mol %)	CuO (mol %)	SnO$_2$ (mol %)	p_{O_2}* (mol %)	Chilled glass colour
CuA	72 SiO$_2$ + 8 RbO + 0.5%wNaF + 10 K$_2$O + 10 Na$_2$O	0.025	–	0.2	Blue
CuB	72 SiO$_2$ + 8 RbO + 0.5%wNaF + 10 K$_2$O + 10 Na$_2$O	0.025	0.0062	0.2	Light blue
CuC	72 SiO$_2$ + 8 RbO + 0.5%wNaF + 10 K$_2$O + 10 Na$_2$O	0.025	0.0125	>0.2	Faint yellowish
CuD	72 SiO$_2$ + 8 RbO + 0.5%wNaF + 10 K$_2$O + 10 Na$_2$O	0.025	0.0250	0.2	Faint yellowish

striking, cuprous oxide is formed from the dissolved Cu$^+$ ions present in the chilled glass, according to the reaction

$$Si-O-Cu^+ + Cu^+-O-Si \rightarrow Si-O-Si + Cu_2O \quad (3)$$
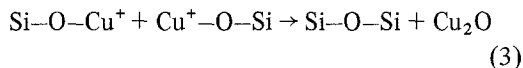
In this case the ruby colour is produced by colloidal cuprous oxide aggregated during the thermal treatment.

The purpose of the present work has been to apply the techniques of luminescence and electron paramagnetic resonance (EPR) to obtain new information about the mechanism ruling the colour development in copper ruby glasses. In fact, Cu$^+$ and Sn^{2+} ions present well-defined emission bands which have been investigated already in a number of glasses [4–6].

On the other hand, Cu^{2+}, having an incomplete 3d^9 electron configuration, induces an EPR spectrum which also is well documented [7–9]. From this study it has been possible to follow the evolution of the redox pairs involved in this process. According to this behaviour a new model for the colouration process, which has sound experimental basis, is proposed.

This work illustrates the potential of spectroscopic techniques to elucidate complex microscopic processes involving redox transformations. A preliminary account of this work has been presented at the XIII International Congress on Glass [10].

2. Experimental details
2.1. Sample preparation
A series of glasses with different additions of CuO and SnO$_2$ were prepared. They were melted in porcelain crucibles in a gas furnace with a controlled atmosphere, at 1550° C for 4 h, bubbling with argon every hour. The compositions are given in Table I.

After different heat treatments, only glasses CuC and CuD developed the ruby colour. Several meltings of glass CuB were made in strongly reducing conditions and none of them did strike.

In the best case reddish brown superficial veins were obtained. The ruby glass CuC was treated at 420° C for 0.25 to 172 h and glass CuD at 360° C for 0.5 to 96 h. The thermal threatments were made in a electric furnace in air and the temperatures chosen were low enough to allow a proper control of the ruby colour development.

2.2. Spectroscopic measurements
Absorption spectra of 0.5 to 1 mm thick polished samples were measured on a Cary 17 spectrophotometer.

Luminescence emission and excitation spectra were obtained with a Jobin–Yvon 543 spectrofluorimeter, using suitable filters and two different types of samples: plane-parallel polished plates and ground glass. These spectra were uncorrected for instrumental parameters such as diffraction-grating efficiency, detector response and source emission intensity.

The EPR spectra of all the glasses studied were determined with a Varian E12 spectrometer operating at microwave frequencies in the X-band ($\sim$ 9 GHz). The powdered glass sample with a particle size between 0.1 and 1 mm was introduced in the resonance cavity of the quartz tube. All the spectra were obtained at room temperature.

3. Experimental results
3.1. Optical absorption
Absorption spectra of copper ruby glasses have been taken at different stages of the colour evolution. Fig. 1 shows the spectrum corresponding to the initial state, the chilled colourless glass, together with those taken after 0.5 and 1 h of annealing at 360° C. In the investigated wavelength range, the initial state does not show any absorption. Copper may be present in the glass as Cu$^+$, Cu^{2+} and Cu^0. The absorption band associated with Cu$^+$ ions should appear near 250 nm [5, 9] from the studied range, but it is masked by the main absorption edge of the material. On the other hand, Cu^{2+} ions are associated with a band about 800 nm [9]. How-
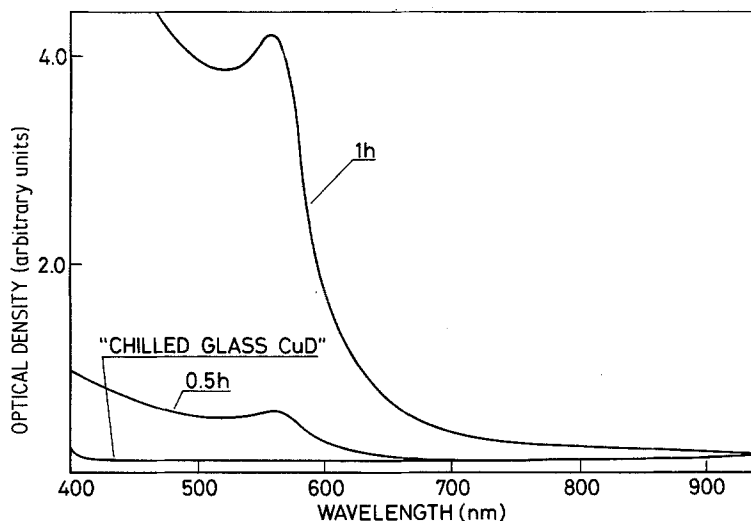
ever, none of these bands has been observed in our glasses.

With striking, a well defined band at 560 nm clearly develops, which is superimposed on a background absorption which increases towards shorter wavelengths. This band has been explained [11] using Mie's theory for colloidal colouration, including the scattering and the specific absorption of the particles.

The optimum ruby colour can be roughly associated with the spectrum obtained after 1 h annealing (Fig. 1). For longer heat treatments, the glass has a livery aspect, the scattering contribution increases and the colour is spoiled.

3.2. Fluorescence
Additional information about ruby colouring process can be obtained through luminescence spectra during annealing treatments.

3.2.1. Assignment of the emission bands
The room temperature (RT) emission spectra for the chilled glasses labelled CuB, CuC and CuD, containing different amounts of tin (see Table I), are displayed in Fig. 2a. The three glasses show two well resolved broad bands peaking at 450 nm (width = 0.65 eV) and 550 nm (0.62 eV), which are, respectively, excited at 250 nm and 310 nm. The relative intensity of the bands changes from glass to glass. The ratio I_{450}/I_{550} between the intensities of both emissions, depends linearly on the ratio $[SnO_2]/[CuO]$ of both oxide concentrations, as can be clearly appreciated from Fig. 2b. It must be noted that the peak position

on the 550 nm emission band appears to have shifted to shorter wavelengths in the CuB and CuC glasses due to overlapping with the 450 nm emission band.

The excitation spectra corresponding to these emission bands are given in Fig. 3. For the 450 nm band, the excitation peaks at 250 nm (after correction for the overlapping shift). The excitation for the 550 nm band has its maximum at 320 nm.

In accordance with Parke and Webb [5], the excitation and emission bands at 250 and 450 nm, respectively, can be associated with the Cu+ ions. This assignment is supported by previous data concerning the location of the Cu+ absorption band in different glasses [12]. On the other hand, the 550 nm emission and its corresponding excitation at 320 nm has to be ascribed to the stannous ions, since its intensity grows proportionally to the amount of tin, and similar bands have been reported by Kirkbright [6] for Sn^{2+} in hydrorombic acid glasses.

3.2.2. Evolution of the fluorescence spectra during striking
The evolution of the fluorescence spectra during the colouring of the CuD glass has been studied. Fig. 4 shows the spectra for three different stages of the striking process, corresponding to the initial state, 1 h and 4 h treatments at 360° C. The most interesting result is the decrease of the ratio I_{550}/I_{450} between the intensities of tin and copper emissions with the colouring process. For longer treatments, both emission bands dissappear.

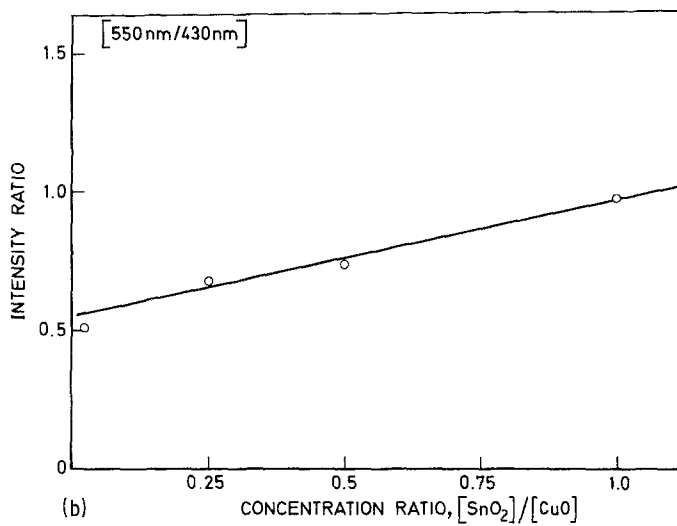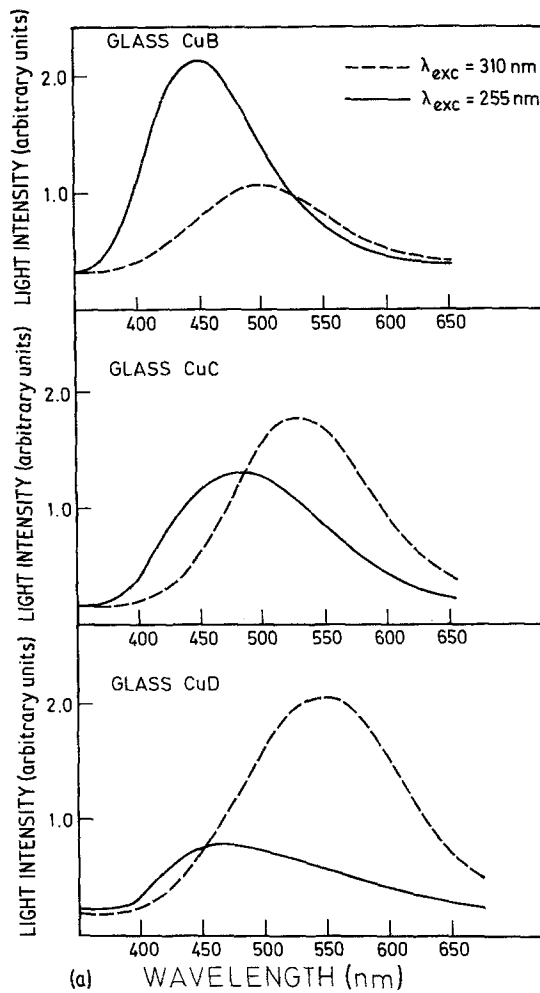It is also worth pointing out that with decrease

Figure 2 (a) RT emission spectra for the CuB, CuC and CuD chilled glasses. (b) Ratio of the intensities of the 550 and 430 nm bands as a function of the concentration ratio [SnO$_2$/CuO].
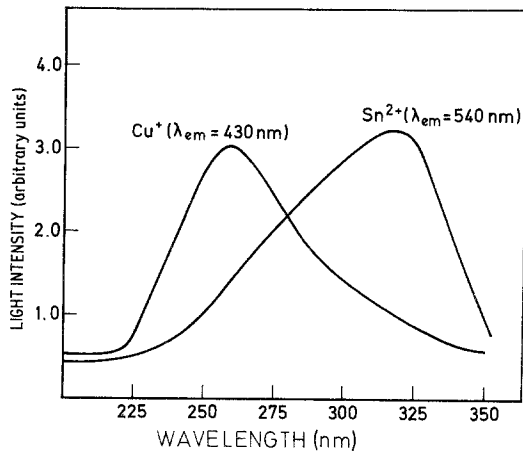
Figure 3 Excitation spectra for the emissions at 450 and 550 nm (fixed emission wavelengths are indicated in the figure).

in the 550 nm band another close band at 600 nm is revealed which may exist in the initial state, but is masked by the dominant 550 nm emission. Indeed, the excitation spectra of the 550 and 600 nm emissions cannot be distinguished, suggesting that the 600 nm band can also be assigned to Sn^{2+} which is in a different lattice configuration. This point would deserve further consideration in future work.

3.3. Electron paramagnetic resonance

The fluorescence spectra have allowed the identification of Cu^+ and Sn^{2+} ions but they do not provide any information about other possible oxidation states.

The EPR technique may be complementary to the optical measurements and it is expected to be particularly useful in investigating the appearance of Cu^{2+} ions. Fig. 5 shows a typical EPR spectrum observed in our copper ruby glasses, very similar to those reported by Imagawa [7] for Cu^{2+} in some borate, silicate and phosphate glasses. It consists of two sets of lines around $g \simeq 2$, with each one containing four peaks.

The observed spectrum was fitted by using the spin Hamiltonian [7]

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y)$$
$$+ A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y)$$

where z is the symmetry axis of the individual copper centers. H_x, H_y and H_z the components of the applied magnetic field and S and I the electron and nuclear spin operators, respectively.
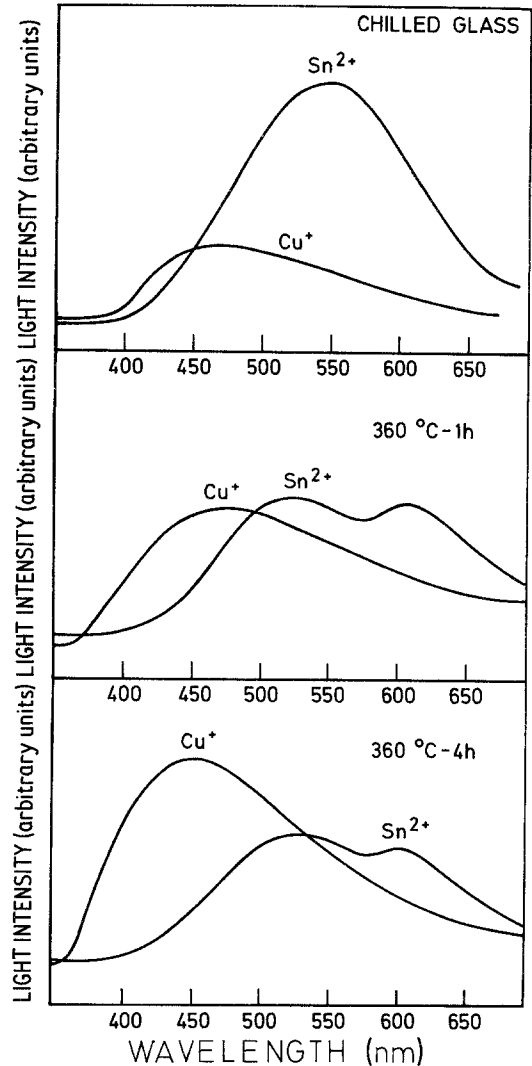

Figure 4 Evolution of the emission spectra for the CuD glass during the striking process (360° C).

The nuclear quadrupole interaction has been neglected. The Hamiltonian parameters obtained from the ruby glasses spectra are: $g_{\parallel} = 2.48$, $g_{\perp} = 2.09$, $|A_{\parallel}| = 160 \times 10^{-4}\,\text{cm}^{-1}$ and $|A_{\perp}| = 23 \times 10^{-4}\,\text{cm}^{-1}$, which are in good agreement with those attributed to Cu^{2+} in a number of oxide glasses [7].

Cu^{2+} concentration in each stage of the striking has been measured by the height of the EPR signal by comparison with a standard glass of known Cu^{2+} content, taking into account that the half-width of the signal stays constant during the thermal treatment. Fig. 6 shows the Cu^{2+} concentration as a function of time, during the striking of glasses CuC and CuD. In the same figure the evolution of the concentration ratio $[Sn^{2+}]/[Cu^+]$,
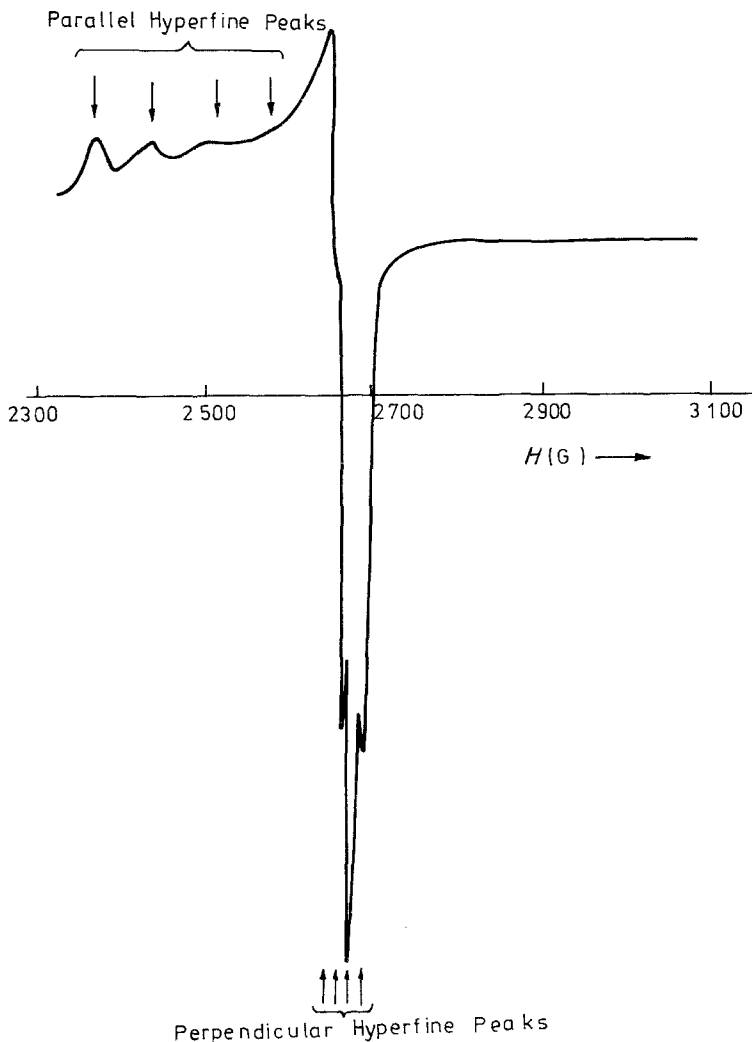
Parallel Hyperfine Peaks

2300   2 500   2 700   2 900   3 100

H (G) $\longrightarrow$

Perpendicular Hyperfine Peaks

obtained from luminescence data, is represented. The chilled colourless glass only contains Cu^{2+} traces ($< 0.01\%$). This concentration level is constant during the first stages of colouration, and rises sharply when the ruby colour develops. The ratio $[Sn^{2+}]/[Cu^+]$ decreases linearly and becomes near null in the same time interval. In other words, the Cu^{2+} concentration starts an abrupt increase after Sn^{2+} concentration has substantially decayed.

It should be mentioned that no spectrum attributable to conduction electrons in metallic particles, like Cu^0 colloids, has been detected. On the other hand, it has neither been possible to detect any change in the Cu^{2+} concentration during thermal treatments in those glasses that did not strike.

4. Discussion

The models proposed to explain the ruby colouration can now be well analysed in the light of the above data.

Reaction (1), involving the Cu^+ reduction and its subsequent thermal aggregation is consistent with the decrease of Cu^+ and Sn^{2+} concentration during striking. However, it does not account for the abrupt growth in Cu^{2+} content after reaching the red ruby colour.

The dismutation reaction 2 proposed by Dietzel [2] agrees with the Cu^+ decrease during the heat treatment. Unfortunately, this model predicts a constant rate for the creation of Cu^{2+} from the beginning, and therefore is at variance with the experimental results shown in Fig. 6. Moreover, the role of tin is not explained in any way.
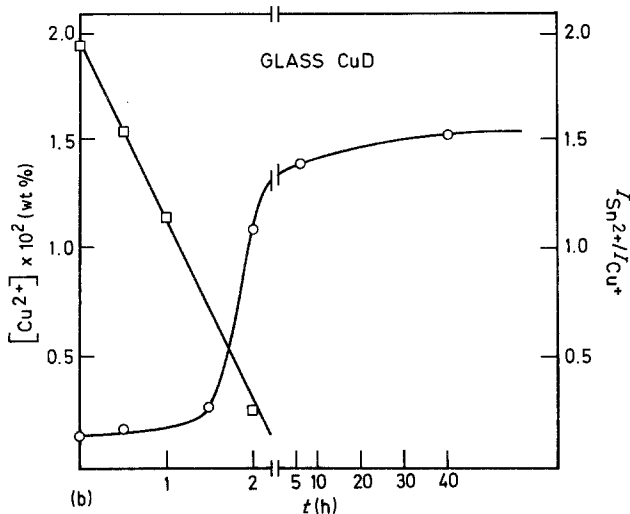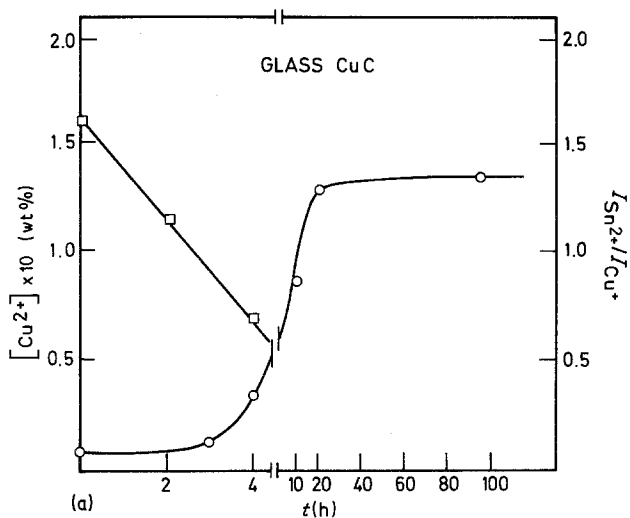
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Figure 6 $[Sn^{2+}]/[Cu^+]$ ratio (□) and $[Cu^{2+}]$ concentration (○) as a function of time during the striking of CuC and CuD glasses.

Finally, reaction 3 cannot explain neither the appearance of Cu^{2+} nor the role played by tin during the striking process.

From the experimental information gathered in this work, a new model is proposed, which can be represented by two simultaneous redox reactions:

$$2Cu^+ \rightarrow Cu^{2+} + Cu^0 \qquad (4)$$

$$2Cu^{2+} + Sn^{2+} \rightarrow 2Cu^+ + Sn^{4+} \qquad (5)$$
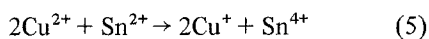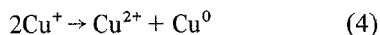
The model accounts for all main features of the data. First, the decrease in the concentration of Cu^+ and Sn^{2+} ions during the striking process is a direct consequence of both reactions. On the other hand, the Cu^{2+} concentration does not increase as long as Sn^{2+} is available as reducing agent. Once all Sn^{2+} ions have become exhausted, the Cu^{2+} content should experience a sharp rise as has been experimentally observed (Fig. 6).

Now, a more detailed picture of the process taking place during the striking of the glass can be given.

In the melting glass, the reduction of Cu^{2+} to Cu^+ leads, under equilibrium conditions, to:

$$\frac{[CuO]}{[Cu_2O]^{1/2}} = k_1(p_{O_2})^{1/4} \qquad (6)$$

which has been experimentally observed for borate and boraluminate glasses by Banerjec and Paul [13].

Under stronger reducing conditions, another equilibrium is set up between the lower oxidation states Cu^+ and Cu^0, which is governed by the equation:

$$\frac{[Cu_2O]^{1/2}}{[Cu^0]} \simeq k_2(p_{O_2})^{1/4} \qquad (7)$$

The reaction constants k_1 and k_2 increase with decreasing temperature as $\exp(-\alpha/T)$ [13].

Because of the high cooling rate and the following thermal treatment at a temperature below that of its transformation range, the glass can be considered as a steady system chilled at a fixed partial oxygen pressure. Therefore Cu^+ and Cu^0 in excess must precipitate, as Cu_2O and metallic copper, to achieve equilibrium [14]. During striking, Cu_2O aggregates and Cu^0 microcrystals are formed. However, at this stage, reactions 4 and 5 are operative. The dismutation produces a decrease of Cu^+ concentration, reducing the rate of growth of Cu_2O colloids, whereas at the same time, Sn^{2+} ions act as a Cu^+ regeneration channel through reaction 5. If, in the initial colourless state of the glass there is enough Sn^{2+}, reactions 4 and 5 will be completed and SnO_2 and Cu^0 clusters will be obtained at the end of the striking process. However, if the initial concentration of Sn^{2+} ions is too low in relation to that of Cu^+, the residual Cu_2O remaining after the complete reduction of Sn^{2+} will be dismutated according to reaction 4. As the Cu_2O content diminishes and finally disappears, the ruby colour spoils and the glass becomes opaque and turns to a livery aspect, very likely due to the growth in number and size of Cu^0 crystals [11]. At the end, SnO_2, CuO and Cu^0 will be obtained. The final amount of Cu^{2+} will be higher, the lower the initial concentration of Sn^{2+}, which is, in turn, governed by temperature and p_{O_2} in the melting atmosphere.

The above mechanism is experimentally supported by the behaviour of glasses CuC and CuD in which, the lower the initial concentration of Sn^{2+}, the greater is the amount of Cu^{2+} ions at the end of the process. Sn^{2+} regenerates Cu^+ ions, acting on a redox buffer. Although, under strictly controlled conditions of temperature and p_{O_2}, it is possible to obtain ruby glasses free of tin [13], its use allows the extension of the temperature and time ranges wherein ruby colouration can be achieved.

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